ONE-POT SYNTESIS OF MENTHOL FROM CITRONELLAL : APPLICATION OF CITRONELLA OIL

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ABSTRACT

Synthesis of menthol ($C_{10}H_{20}O$) from citronellal ($C_{10}H_{18}O$) has been performed by a one-pot process. The process was conducted in a 250 mL capacity autoclave with acidified natural zeolite and Raney Nickel as catalysts at temperature 120°C, pressure 5 bar, and variation of time 1-8 hours. Natural zeolite and Raney Nickel were placed in the autoclave and it was found that the cyclisation and hydrogenation reaction to form menthol could undergo in the same reactor. FTIR Analysis showed peak formation at 3346.50 cm^{-1} indicating –OH group was formed. Result of ^{1}H-NMR and ^{13}C-NMR analysis reports chemical shifts at δ=71.53 ppm and δ=4.05 ppm. Gas chromatography analysis showed that the conversion was 80% with concentration of menthol about 68% (v/v).

Keywords : menthol, citronellal, one-pot reaction, citronella oil.

INTRODUCTION

Menthol ($C_{10}H_{20}O$) is widely used in cosmetics, pharmaceuticals, toothpastes, chewing gums, and also cigarettes. Currently, synthetic menthol is produced commercially in the world by two companies, Haarman & Reimer and Takasago Corp. In the Haarman & Reimer process racemic (±)-menthols are obtained by hydrogenation of thymol, where as Takasago Corp. developed an asymmetric synthesis technology for producing (-)-menthol from myrcene. Considerable effort have been devoted to the production of menthol by synthetic means from other more readily renewable raw materials and simplify the process into a one-pot process with the help of a selected catalyst.

Citronella oil is a potential renewable material for the development of fine chemicals. The oil is used extensively as a source of important perfumery chemicals like citronellal, citronellol and geraniol, which find extensive use in soap, perfumery, cosmetic and flavoring industries throughout the world (Guenther. E., 1998). Citronella oil is classified in trade into two types : Ceylon citronella oil, obtained from *Cymbopogon nardus Rendle*, is the inferior type, while Java type citronella oil obtained from *Cymbopogon winterianus Jowitt*, is considered superior (Hardjono, 2002)

The synthesis of menthol from citronellal is generally carried out through the selective isomerisation of citronellal to the cyclic alcohol, isopulegol, on acid catalysts. Classically, this cyclization is carried out in protonic media, such as formic acid, phosphoric acid, acetic anhydride, or solid catalysts. Ohloff (1965) has shown that thermal cyclization occurs acidic cleanly and in high yield. The resultant isopulegol isomers formed possess the necessary asymmetric center at C-1 of the p-menthane skeleton for (-)-menthol production.

The unsaturated alcohol is then separated from the reaction mixture and hydrogenated to the corresponding saturated alcohol, menthol (Misono and Noijri, 1990). Hydrogenation is performed in presence of a catalyst. Raney nickel is used in a large number of industrial processses and in organic synthesis because of its stability and high catalytic activity at room tempe-rature. It is typically used in the reduction of compounds that have multiple bonds, such as alkynes, alkenes, nitriles, dienes, aromatics, and carbonyls (http://en.wikipedia.org/wiki/Raney_nikel, 2007).

Milone *et al*. (1999) conducted isomerization of citronellal under mild condition on ZnX_2 (X= Cl, Br, NO3) supported on high surface area and yielded 85% menthol. The research continued on selective one step synthesis of (−)menthol from (C)citronellal on Ru supported on modified SiO_2. Menthol was also developed by enzymatic cleavage. With this method, menthol was produced from menthyl derivatives (Gatfield *et al*., 2002). Schlemenat *et al*. (2002) reported preparation of menthol by catalytic isomerization of D-menthol at temperatures from 30 to 120ºC and pressure of 50 mbar to 300 mbar. The process was in presence of a supported (Al_2O_3) rutherium catalyst.

Citronella oil is easily found in many local markets. Synthesis of menthol from citronellal will increase the value of citronella oil and take part in the development of renewable raw materials. The use of other catalysts substituting expensive ruthenium catalyst for the one-step process will be very beneficial for both laboratory work and industrial application. The aim of this research is to synthesize menthol from Java type citronella oil in the presence of acidified natural zeolite and Raney Nickel catalyst by one-pot reaction method.

EXPERIMENTAL

Citronella oil was obtain from Gunung Halu, West Java and fractionated by bench scale vacuum distillation (60 mmHg) yielding 85% (v/v) citronellal. Acid zeolite was prepared by treating natural zeolite in sulfuric acid and dried in room temperature. For hydrogenation, Raney Nickel (MERCK-Schuchardt) was used. Citronellal was applied in a 200 ml capacity autoclave with the catalyst above and heated until 100ºC. The temperature was kept constant for 3 hours. Hydrogen gas was then flowed for the following 5 hours with a constant pressure of 5 bar and 120ºC. The product was separated from the catalyst and dried by adding anhydrous sodium sulfate.

Analysis of the product was conducted by FTIR (IR Prestige-21, SHIMADZU), ^{1}H-NMR, ^{13}C-NMR (NMR spectroscopy JEOL, ECA 450, 500 MHz), and Gas Chromatography (SHIMADZU, HP-Innowax 0.25mm,30mm).

RESULTS AND DISCUSSION

Analysis of Product

The product of one-pot menthol synthesis was analyzed by FTIR, ^{1}H-NMR, ^{13}C-NMR and gas chromatography techniques. FTIR analysis was conducted for the preliminary analysis to observe the formation of functional group desired. In this case, the formation of alcohol group –OH substituting the carbonyl group of citronellal. FTIR result is shown in Fig 1.

The top part of the figure is the chromatogram of the starting material, namely citronellal, and the bottom is the menthol product formed. From the result, it is observed in the starting material that there was absorption at 1726.29 cm^{-1} showing the occurrence of an aldehyde group. Meanwhile at the product, this absorption was no longer observed and showed a new absorption at 3346.50 cm^{-1} indicating a –OH group has been formed. This shows that cyclisation of citronellal has occurred preparing an alcoholic molecule as the product. Alkene functional group can also be an indicator of the reaction. It is shown in the chromatogram that there is a presence of C=C group in citronellal and at around 1620 cm^{-1}. This reports that hydrogenation has been successful and menthol was produced.

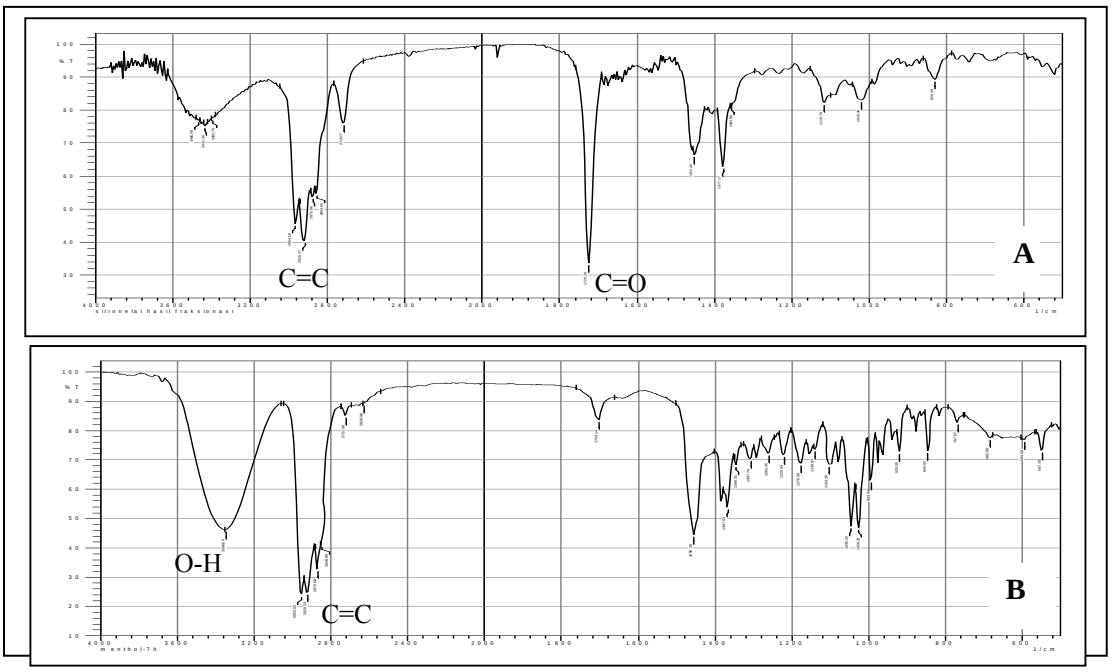

Fig. 1 FTIR analysis (IR Prestige-21, SHIMADZU) of citronellal (A) and menthol (B)

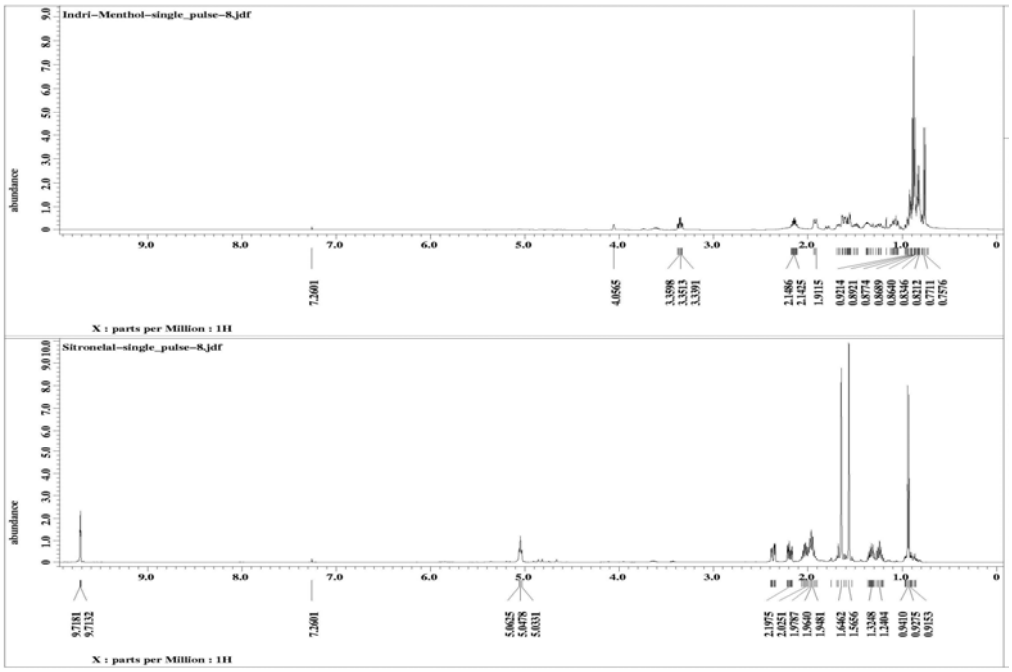

Fig. 2 [1]H-NMR of menthol (A) and citronellal (B)

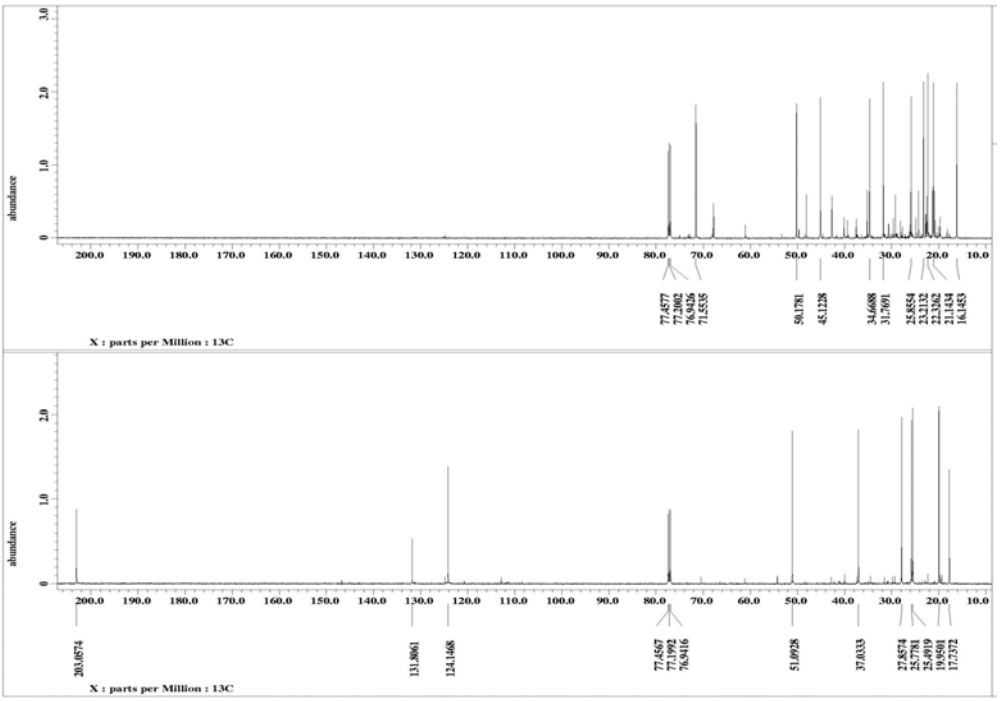

Fig.3 [13]C-NMR of menthol (A) and citronellal (B)

Overlay of [1]H-NMR analysis for menthol and citronellal is shown in Fig. 2. [1]H-NMR analysis was conducted using chloroform as the solvent. Difference in chemical shift (δ) of the starting material citronellal and product menthol was observed. Citronellal structure gave δ=9.71 ppm which indicated a proton in the environment of C=O group and δ=5.04 ppm representing a proton in C=C group. This does not occur in the product and a new shift at δ=4.05 ppm was formed. This chemical shift is due to the –OH formation in the menthol structure.

Fig. 3 reports analysis of [13]C-NMR. This analysis also proves that menthol was produced, where δ=203.06 (C=O), δ=131.81 and δ =124.15

ppm (C=C) is no longer observed. A new shift at 71.53 ppm was formed indicating deshielding due to the carbon on oxygen of the –OH group.

To measure the concentration of menthol, gas chromatography analysis was performed. Gas chromatography showed a new peak at retention time of 34-36 minutes, indicating that menthol has been formed following the disappearance of citronellal at 20-22 minutes and isopulegol at 24-26 minutes. The concentration of menthol produced was 68% (v/v).

Effect of Catalyst

Citronellal produced from fractionation was 85% (v/v). The remaining 15% mainly contained other major compounds of citronella oil, citronellol and geraniol. Synthesis of menthol from citronellal includes two reactions steps, which are citronellal isomerization to isopulegol, continued with isopulegol hydrogenation to menthols, respectively. The reaction involved interaction of positive ions in the lewis acid site of zeolite followed by hydrogenation on the surface of Raney Nickel catalyst. Reaction is shown in Fig. 4.

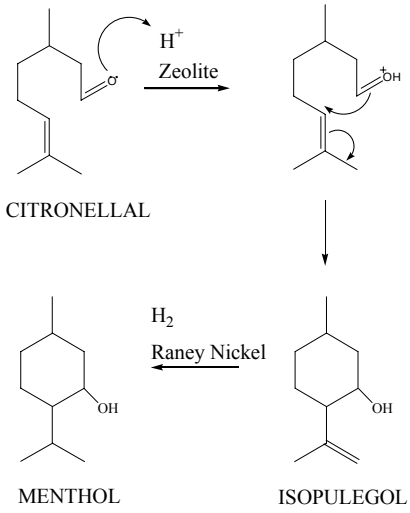

Fig. 4 Synthesis of menthol from citronellal

Formation of isopulegol was propagated by the active lewis acid site of zeolite catalyst. The presence of lewis acid site results in a lower energy activation for the cyclisation of citronellal. Zeolite are basically hydrated alumino-silicate minerals with an open structure that can accommodate a wide variety of positive ions, in this case H^+. These ions influenced the stability of carbonyl group in the citronellal structure. The carbonyl group of citronellal donates a pair of electron to the carbon atom resulting cyclisation. Hydrogen was flowed in the next step and it was found that Raney Nickel performed its activity in the hydrogenation although it was placed in the same unit in with zeolite catalyst from the beginning of the process. The alkene bond in isopulegol was then reduced yielding the desired menthol.

Effect of Time

Fig. 5 reports products formed during the process. Concentration of citronellal at the beginning of the process was recorded at 85% (v/v). It can be observed that as time increases, concentration of citronellal decreases from the starting point (t=0h). At t=3h, concentration of citronella was found 20% (v/v) and dropped to 0% (v/v) at t=6h. This indicated that cyclisation has occurred, where citronellal was transformed to isopulegol. Isopulegol produced drastically during the first 4 hours yielding about 67% (v/v). For the following 4 hours, concentration of isopulegol decreased and dropped to 15% (v/v). Hydrogenation performed from the forming alcohol and the desired menthol was produced. Concentration of menthol increased from 0% (v/v) at t=3 to 68% (v/v) at the final hour. At this point it was observed that menthol was successfully produced from isopulegol.

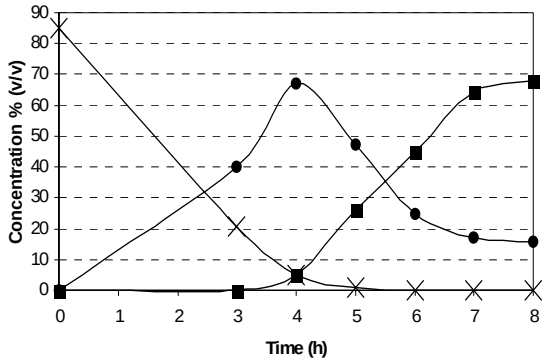

Fig. 5. Products during menthol synthesis from citronellal: (X) citronellal, (•) isopulegol, (■) menthol

Conversion of Citronellal to Menthol

Conversion to menthol is shown in Fig. 6. It was found that synthesis of menthol using both lewis acid and hydrogenation catalyst can undergo in the same reactor (one-pot reaction), where the two catalysts was placed together. Conversion of menthol increased during the process. The first menthol produced was at t=3h. This indicates that at the first 3 hours, the lewis acid was dominant in the reaction to form isopulegol. For the following hours, isopulegol was hydrogenated by Raney nickel and at the end 80% conversion was observed. Conversion was calculated by dividing the concentration of menthol yielded (68%) towards concentration of the starting

citronellal (85%). The result was then converted to percentage. Concentration of both citronellal and menthol was obtained by Gas Chromatography measurement.

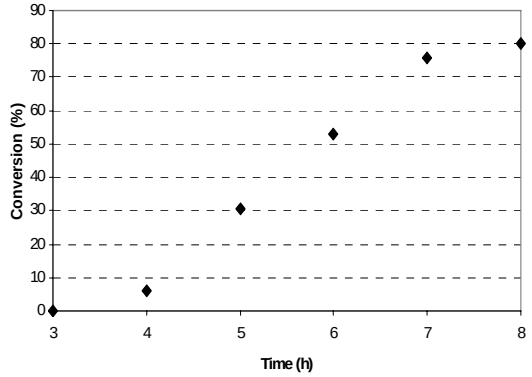

Fig. 6. Formation of menthol from citronellal vs. time

CONCLUSION

This study pointed out the possibility of menthol synthesis from citronellal fractionated from citronella oil by a one-pot reaction method. Synthesis occurred in the same reactor with two reaction steps, which are citronellal isomerization to isopulegol, and isopulegol hydrogenation to menthols, respectively. The reaction occurred in presence of acidified natural zeolite and Raney Nickel catalyst. Process of Java type citronella oil at 120ºC, 5 bar and 8 hours yielded 80% conversion with 68% (v/v) concentration of menthol.

Acknowledgement

Funding from the Government of Indonesia (2005 DIP Project) and cooperation from Process Technology and Synthesis for Essential Oil Research Group at The Research Centre for Chemistry, Indonesian Institute of Sciences is gratefully acknowledged.

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